22/25(a)

The University of Sydney

CHEM1405 - CHEMISTRY (VETERINARY SCIENCE)

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2008 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		**SID NUMBER**	
OTHER NAMES		**TABLE NUMBER**	

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 21 pages of examinable material.
- Complete the written section of the examination paper in **INK.**
- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.
- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.
- Each new short answer question begins with a •.
- Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.
- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheet.
- Pages 13 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-8	25	

Short answer section

Page	Marks Max	Gained		Marker
9	5			
10	4			
11	4			
12	6			
14	4			
15	6			
16	4			
17	5			
18	10			
19	5			
20	7			
21	4			
22	7			
23	4			
Total	75			

- In the spaces provided, explain the meanings of the following terms.

Marks
3

(a) enzyme

(b) cofactor

(c) peptide

- Explain, in terms of chemical bonding and intermolecular forces, the following trend in melting points: $CH_4 < I_2 < NaCl <$ silica (SiO_2)

2

	Marks
• What is the bond order of the nitrogen-oxygen bonds in the nitrate ion, NO_3^-? Explain your answer.	**2**
• The observed geometry of the atoms attached to the N atom in H_2NCOCH_3 is trigonal planar. Explain this observation.	**2**

	Marks
• Give the ground-state electron configuration of the aluminium atom.	**2**
Provide one set of valid quantum numbers (n, l, m_l, m_s) for the highest energy electron.	
• The osmotic pressure of a solution containing 5.5 g L^{-1} of a polypeptide is 0.103 atm at 5 °C. Calculate the molar mass of the polypeptide.	**2**
Answer:	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 6

- A galvanic cell is made of a Ni^{2+}/Ni half cell with $[Ni^{2+}] = 1.00 \times 10^{-3}$ M and a Ag^{+}/Ag half cell with $[Ag^{+}] = 5.00 \times 10^{-2}$ M. Calculate the electromotive force of the cell at 25 °C.

Answer:

Calculate the equilibrium constant of the reaction at 25 °C.

Answer:

Calculate the standard free energy change of the reaction at 25 °C.

Answer:

Indicate whether the reaction is spontaneous or not. Give reasons for your answer.

Express the overall reaction in the shorthand voltaic cell notation.

Marks 4

- Calculate ΔG^o for the following reaction at 25 °C.

$$5SO_3(g) + 2NH_3(g) \rightarrow 2NO(g) + 5SO_2(g) + 3H_2O(g)$$

Data:

	S^o / J K^{-1} mol^{-1}	$\Delta_f H°$ / kJ mol^{-1}
$SO_3(g)$	256.2	–395.2
$NH_3(g)$	192.5	–46.19
NO(g)	210.6	90.37
$SO_2(g)$	248.5	–296.9
$H_2O(g)$	188.7	–241.8

Answer:

Is the reaction spontaneous? Give a reason for your answer.

At what temperature does the spontaneity change?

Answer:

Marks

- Explain why copper dissolves in dilute HNO_3, but not in dilute HCl? **2**

- Nitrous oxide decomposes at 25 °C according to the following equation. **4**

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g) \qquad K_p = 1.8 \times 10^{36}$$

What is the value for K_p at 40 °C?

Answer:

Is the reaction endothermic or exothermic? Give a reason for your answer.

Marks 4

- Phosgene is a toxic gas prepared by the reaction of carbon monoxide with chlorine.

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

The following data were obtained in a kinetics study of its formation at 150 °C.

Experiment	Initial [CO] (mol L^{-1})	Initial [Cl_2] (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
1	1.00	0.100	1.29×10^{-3}
2	0.100	0.100	1.33×10^{-4}
3	0.100	1.00	1.30×10^{-3}
4	0.100	0.0100	1.32×10^{-5}

Write the rate law for the formation of phosgene at 150 °C.

Calculate the value of the rate constant at 150 °C.

Answer:

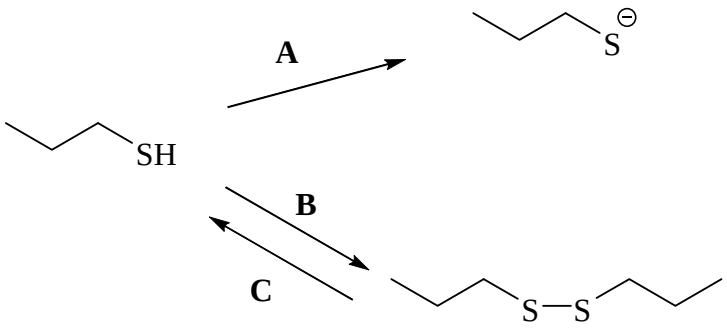
Calculate the rate of appearance of phosgene when [CO] = [Cl_2] = 1.3 M.

Answer:

	Marks
• Codeine, a cough suppressant extracted from crude opium, is a weak base with a pK_b = 5.79. What is the pH of a 0.020 M solution of codeine?	**2**
Answer:	
• A buffer solution is formed with 0.250 M CH_3COOH and 0.350 M CH_3COONa. What is the pH of this buffer solution? (K_a of acetic acid = 1.8×10^{-5} M.)	**3**
Answer:	
Calculate the pH of the solution formed when 6.3×10^{-2} mol of NaOH is added to 1.0 L of the buffer solution.	
Answer:	

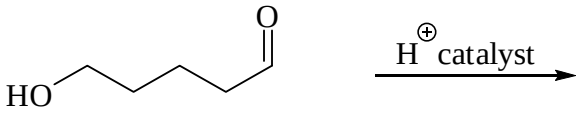
Marks

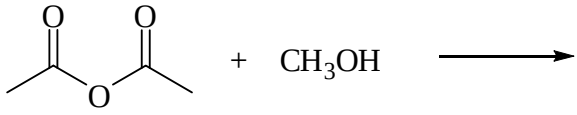
- Indicate the reagents used in the laboratory to undertake the following transformations. **3**

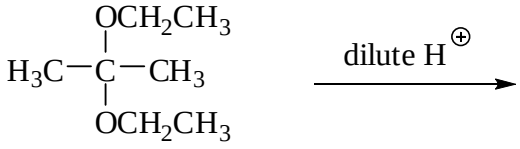


A:	
B:	
C:	

- Draw the constitutional formula(s) of the major organic product(s) of the following reactions. **7**

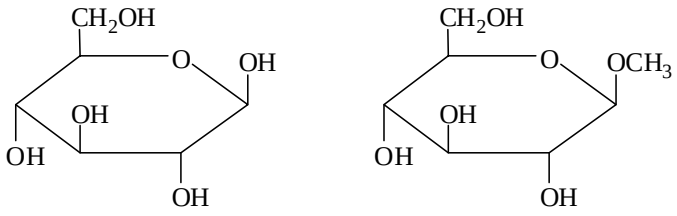




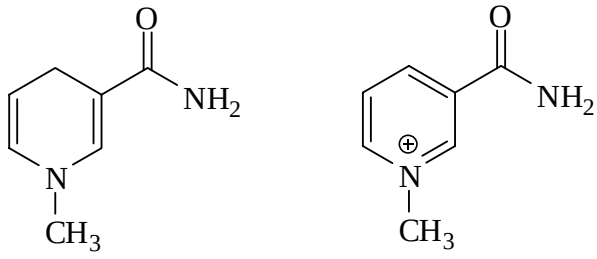
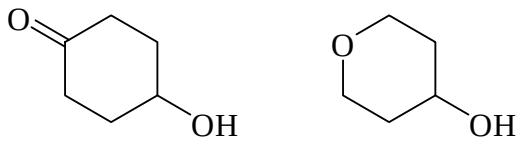


Marks 5

- Using a chemical test, how would you distinguish between the following pairs of compounds? Indicate the reagent you would use and the observations you would make.

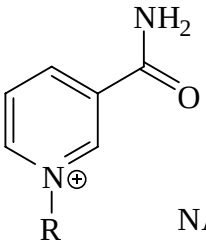
Compounds	Reagent and observation
	
	
	

Using a spectroscopic technique, how would you distinguish between the following pairs of compounds? Indicate the observations you would make.

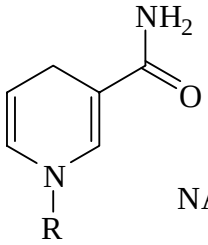
Compounds	Technique and observation
	
	

Marks 7

- NAD^+/NADH is a biological redox system. The two species may be represented by the structures below.



NAD^+



NADH

What are the requirements for a compound to be aromatic? Indicate which of NAD^+ and/or NADH fulfil these requirements.

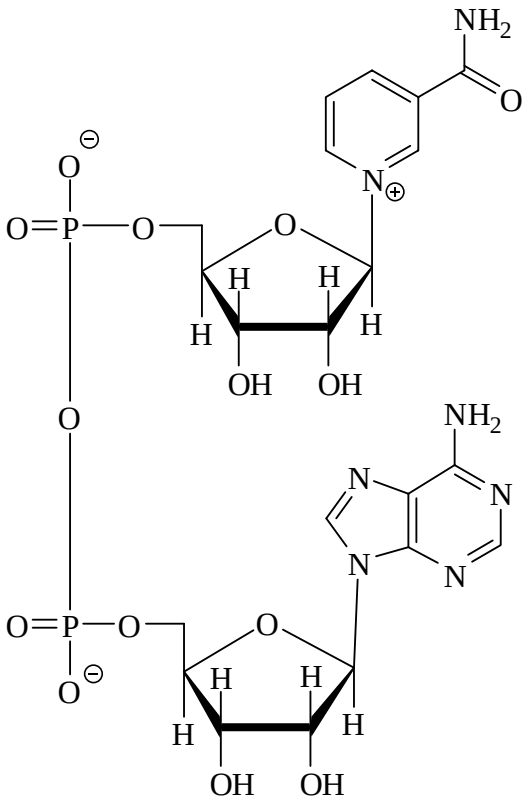
Which of NAD^+ and/or NADH will react with cold dilute H^+ in an acid/base reaction? Using the structures above, give the chemical equation for the reaction and a brief explanation for your choice.

Draw the structure of a tautomer of NADH.

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks 4

The full structure of NAD^+ contains ribose, two phosphate groups and adenine.

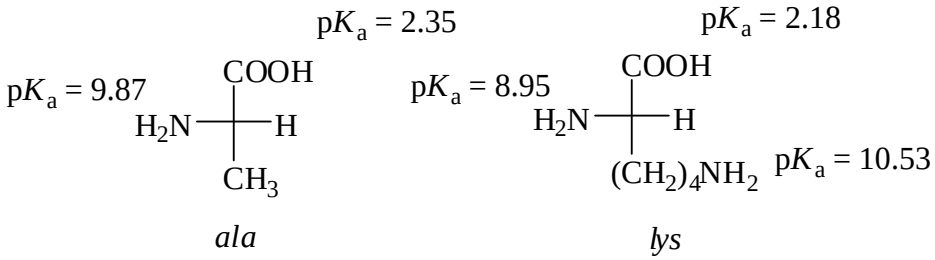


Draw ribose as a Fischer projection.

Adenine is also a component of DNA used in forming complementary strands by hydrogen bonding. Indicate the sites of hydrogen bonding on adenine that are used in forming complementary strands in DNA and differentiate between those sites that are hydrogen bond donors and those that are hydrogen bond acceptors.

Marks 7

- Alanine (*ala*) and lysine (*lys*) are two amino acids with the structures given below as Fischer projections. The pK_a values of the conjugate acid forms of the different functional groups are indicated.



ala *lys*

Draw the structure of the dipeptide *ala-lys* in its zwitterionic form.

Would you expect the dipeptide to be soluble in water? Give a brief reason for your choice.

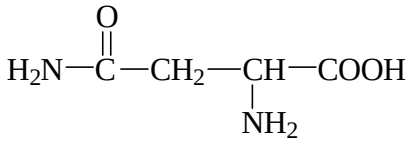
Would you expect the dipeptide to be acidic, neutral or basic? Give a brief reason for your choice.

Estimate the isoelectric point of the dipeptide.

Marks 4

- The amino acid, asparagine, was isolated from asparagus juice in 1806. The uncharged form, **Y**, is given below.

Y



Draw the constitutional formula of the product(s) formed in the reaction of **Y** with the following reagents.

Cold, dilute hydrochloric acid	Cold, dilute sodium hydroxide
Hot, 6 M hydrochloric acid	Hot, 6 M sodium hydroxide

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DATA SHEET

Physical constants

Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}

Faraday constant, $F = 96485$ C mol^{-1}

Planck constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light in vacuum, $c = 2.998 \times 10^{8}$ m s^{-1}

Rydberg constant, $E_R = 2.18 \times 10^{-18}$ J

Boltzmann constant, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

Permittivity of a vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1}

Gas constant, $R = 8.314$ J K^{-1} mol^{-1}

$= 0.08206$ L atm K^{-1} mol^{-1}

Charge of electron, $e = 1.602 \times 10^{-19}$ C

Mass of electron, $m_e = 9.1094 \times 10^{-31}$ kg

Mass of proton, $m_p = 1.6726 \times 10^{-27}$ kg

Mass of neutron, $m_n = 1.6749 \times 10^{-27}$ kg

Properties of matter

Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L

Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L

Density of water at 298 K = 0.997 g cm^{-3}

Conversion factors

1 atm = 760 mmHg = 101.3 kPa

0 °C = 273 K

1 L = 10^{-3} m^3

1 Å = 10^{-10} m

1 eV = 1.602×10^{-19} J

1 Ci = 3.70×10^{10} Bq

1 Hz = 1 s^{-1}

1 tonne = 10^3 kg

1 W = 1 J s^{-1}

Decimal fractions

Fraction	Prefix	Symbol
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Decimal multiples

Multiple	Prefix	Symbol
10^3	kilo	k
10^6	mega	M
10^9	giga	G

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Standard Reduction Potentials, E°

Reaction	$E°$ / V
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.18
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+0.96
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–0.89
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.68
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.36
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04

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Useful formulas

Quantum Chemistry

$E = h\nu = hc/\lambda$

$\lambda = h/mv$

$E = -Z^2E_R(1/n^2)$

$\Delta x \cdot \Delta(mv) \geq h/4\pi$

$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$

$4.5k_BT = hc/\lambda$

$T = 2.898 \times 10^6/\lambda(\text{nm})$

Electrochemistry

$\Delta G° = -nFE°$

Moles of $e^- = It/F$

$E = E° - (RT/nF) \times 2.303 \log Q$

$= E° - (RT/nF) \times \ln Q$

$E° = (RT/nF) \times 2.303 \log K$

$= (RT/nF) \times \ln K$

$E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

Gas Laws

$PV = nRT$

$(P + n^2a/V^2)(V - nb) = nRT$

Colligative properties

$\pi = cRT$

$P_{solution} = X_{solvent} \times P°_{solvent}$

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Kinetics

$t_{½} = \ln 2/k$

$k = Ae^{-Ea/RT}$

$\ln[A] = \ln[A]_o - kt$

$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Radioactivity

$t_{½} = \ln 2/\lambda$

$A = \lambda N$

$\ln(N_0/N_t) = \lambda t$

^{14}C age $= 8033 \ln(A_0/A_t)$ years

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$K_p = K_c (RT)^{\Delta n}$

Miscellaneous

$A = -\log \frac{I}{I_0}$

$A = \varepsilon cl$

$E = -A \frac{e^2}{4\pi\varepsilon_0 r} N_A$

Mathematics

If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 HYDROGEN **H** 1.008																	2 HELIUM **He** 4.003
3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012											5 BORON **B** 10.81	6 CARBON **C** 12.01	7 NITROGEN **N** 14.01	8 OXYGEN **O** 16.00	9 FLUORINE **F** 19.00	10 NEON **Ne** 20.18
11 SODIUM **Na** 22.99	12 MAGNESIUM **Mg** 24.31											13 ALUMINIUM **Al** 26.98	14 SILICON **Si** 28.09	15 PHOSPHORUS **P** 30.97	16 SULFUR **S** 32.07	17 CHLORINE **Cl** 35.45	18 ARGON **Ar** 39.95
19 POTASSIUM **K** 39.10	20 CALCIUM **Ca** 40.08	21 SCANDIUM **Sc** 44.96	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.94	24 CHROMIUM **Cr** 52.00	25 MANGANESE **Mn** 54.94	26 IRON **Fe** 55.85	27 COBALT **Co** 58.93	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.55	30 ZINC **Zn** 65.39	31 GALLIUM **Ga** 69.72	32 GERMANIUM **Ge** 72.59	33 ARSENIC **As** 74.92	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.90	36 KRYPTON **Kr** 83.80
37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62	39 YTTRIUM **Y** 88.91	40 ZIRCONIUM **Zr** 91.22	41 NIOBIUM **Nb** 92.91	42 MOLYBDENUM **Mo** 95.94	43 TECHNETIUM **Tc** [98.91]	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.91	46 PALLADIUM **Pd** 106.4	47 SILVER **Ag** 107.87	48 CADMIUM **Cd** 112.40	49 INDIUM **In** 114.82	50 TIN **Sn** 118.69	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.90	54 XENON **Xe** 131.30
55 CAESIUM **Cs** 132.91	56 BARIUM **Ba** 137.34	57-71	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.95	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.2	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.09	79 GOLD **Au** 196.97	80 MERCURY **Hg** 200.59	81 THALLIUM **Tl** 204.37	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.98	84 POLONIUM **Po** [210.0]	85 ASTATINE **At** [210.0]	86 RADON **Rn** [222.0]
87 FRANCIUM **Fr** [223.0]	88 RADIUM **Ra** [226.0]	89-103	104 RUTHERFORDIUM **Rf** [261]	105 DUBNIUM **Db** [262]	106 SEABORGIUM **Sg** [266]	107 BOHRIUM **Bh** [262]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [266]	110 DARMSTADTIUM **Ds** [271]	111 ROENTGENIUM **Rg** [272]							

LANTHANIDES	57 LANTHANUM **La** 138.91	58 CERIUM **Ce** 140.12	59 PRASEODYMIUM **Pr** 140.91	60 NEODYMIUM **Nd** 144.24	61 PROMETHIUM **Pm** [144.9]	62 SAMARIUM **Sm** 150.4	63 EUROPIUM **Eu** 151.96	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.93	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.93	70 YTTERBIUM **Yb** 173.04	71 LUTETIUM **Lu** 174.97
ACTINIDES	89 ACTINIUM **Ac** [227.0]	90 THORIUM **Th** 232.04	91 PROTACTINIUM **Pa** [231.0]	92 URANIUM **U** 238.03	93 NEPTUNIUM **Np** [237.0]	94 PLUTONIUM **Pu** [239.1]	95 AMERICIUM **Am** [243.1]	96 CURIUM **Cm** [247.1]	97 BERKELLIUM **Bk** [247.1]	98 CALIFORNIUM **Cf** [252.1]	99 EINSTEINIUM **Es** [252.1]	100 FERMIUM **Fm** [257.1]	101 MENDELEVIUM **Md** [256.1]	102 NOBELIUM **No** [259.1]	103 LAWRENCIUM **Lr** [260.1]